



The Effects of Acid Passivation, Tricresyl Phosphate Presoak, and UV/Ozone Treatment on the Tribology of Perfluoropolyether-Lubricated 440C Stainless Steel Couples

Bradley A. Shogrin
Jet Propulsion Laboratory, Pasadena, California

William R. Jones, Jr.
Glenn Research Center, Cleveland, Ohio

Pilar Herrera-Fierro
Energy Conversion Devices, Troy, Michigan

Mark J. Jansen
AYT Corporation, Brook Park, Ohio

The NASA STI Program Office . . . in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the Lead Center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- **TECHNICAL PUBLICATION.** Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA's counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.
- **TECHNICAL MEMORANDUM.** Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.
- **CONTRACTOR REPORT.** Scientific and technical findings by NASA-sponsored contractors and grantees.

- **CONFERENCE PUBLICATION.** Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or cosponsored by NASA.
- **SPECIAL PUBLICATION.** Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.
- **TECHNICAL TRANSLATION.** English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized data bases, organizing and publishing research results . . . even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at <http://www.sti.nasa.gov>
- E-mail your question via the Internet to help@sti.nasa.gov
- Fax your question to the NASA Access Help Desk at 301-621-0134
- Telephone the NASA Access Help Desk at 301-621-0390
- Write to:
NASA Access Help Desk
NASA Center for AeroSpace Information
7121 Standard Drive
Hanover, MD 21076



The Effects of Acid Passivation, Tricresyl Phosphate Presoak, and UV/Ozone Treatment on the Tribology of Perfluoropolyether-Lubricated 440C Stainless Steel Couples

Bradley A. Shogrin
Jet Propulsion Laboratory, Pasadena, California

William R. Jones, Jr.
Glenn Research Center, Cleveland, Ohio

Pilar Herrera-Fierro
Energy Conversion Devices, Troy, Michigan

Mark J. Jansen
AYT Corporation, Brook Park, Ohio

Prepared for the
Second World Tribology Congress
sponsored by The Society of Tribologists and Lubrication Engineers
Vienna, Austria, September 3-7, 2001

National Aeronautics and
Space Administration

Glenn Research Center

Trade names or manufacturers' names are used in this report for identification only. This usage does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

This report is a preprint of a paper intended for presentation at a conference. Because of changes that may be made before formal publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

Available from

NASA Center for Aerospace Information
7121 Standard Drive
Hanover, MD 21076

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22100

Available electronically at <http://gltrs.grc.nasa.gov/GLTRS>

THE EFFECTS OF ACID PASSIVATION, TRICRESYL PHOSPHATE PRE-SOAK, AND UV/OZONE TREATMENT ON THE TRIBOLOGY OF PERFLUOROPOLYETHER-LUBRICATED 440C STAINLESS STEEL COUPLES

Bradley A. Shogrin
National Aeronautics and Space Administration
Jet Propulsion Laboratory
Pasadena, California 91109

William R. Jones, Jr.
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Pilar Herrera-Fierro
Energy Conversion Devices
Troy, Michigan 48404

Mark J. Jansen
AYT Corporation
Brook Park, Ohio 44142

ABSTRACT

The boundary-lubrication performance of two perfluoropolyether (PFPE) thin films in the presence of passivated 440C stainless steel is presented. The study used a standard ball on disk (BoD) tribometer in dry nitrogen and a vacuum spiral orbit tribometer (SOT). Stainless steel surfaces were passivated with one of four techniques: high and low temperature chromic acid bath, a tricresyl phosphate (TCP) soak, or UV/Ozone treated for 15 minutes. After passivation, each BoD disk had a 400Å film of Krytox 16256 (PFPE) applied to it. The lifetimes of these films were quantified by measuring the number of sliding cycles before an increase in friction occurred. The lubricated lifetime of the 440C couple was not altered as a result of the various passivation techniques. The resulting surface chemistry of each passivation technique was examined using X-ray photoelectron spectroscopy (XPS). The SOT was used to examine the effects of the TCP treatment on the lubricated lifetime of another PFPE, Brayco 815Z, under rolling conditions. None of the passivation techniques were found to dramatically increase the oxide film thickness or lubricated lifetimes.

INTRODUCTION

Pretreatment of instrument-bearing components with either a tricresyl phosphate (TCP) presoak [1-10] or a chromic acid passivation bath [2,4], has been performed for over 30 years. It has been repeatedly shown that these pretreatment procedures improve the bearing's performance in low-speed, boundary lubricated contacts [1,2,9,10]. Over the years, these pretreatments have been incorporated in standard bearing component preconditioning procedures in an attempt to provide additional protection while in boundary lubrication conditions [2,8]. However, all known reports of improved boundary lubrication performance have used either mineral oils or synthetic esters. This is

not surprising since the vast majority of TCP and chromic acid passivation research was performed in the 1960's, when these were the dominant classes of lubricants. These lubricant classes are vastly different than the perfluoropolyether class commonly used today. There has only been one study [11] that focused on the longevity of a TCP passivated surface lubricated with Krytox, a PFPE, and none on chromic acid passivated surfaces. Wedeven et al. [11] concluded that TCP passivation had no effect on the longevity of the PFPE lubricated system.

Perfluoropolyethers (PFPEs) have been the preferred liquid lubricants for space applications for over three decades because of their proven

tribological performance and other attractive properties [12] including low vapor pressure, low chemical reactivity, and wide liquid temperature range. PFPEs are used in many space mechanisms including actuators, antenna pointing mechanisms, filter wheels, gyroscopes, and scanning mirrors [13,14]. However, there have been many incidents during which PFPE lubricated components have shown anomalous behavior [15,16]. These anomalies are thought to be the result of PFPE degradation. In order to understand how various passivation techniques might affect the boundary lubricating performance of PFPEs, it is first necessary to understand how PFPEs degrade.

Several studies have focused on modeling the degradation of PFPE lubricants. Research has repeatedly shown that PFPEs degrade while in boundary lubricated, sliding/rolling contact [17-22] and at elevated temperatures [23-26], losing their desirable properties, including lubricity. Although few models have been proposed to explain the degradation, it has been shown that the rate of degradation is dependent upon the substrate surface chemistry and the presence and relative strength of Lewis acids.

Kasai [23] has shown that the thermal catalytic degradation of a PFPE is dependent upon the strength of the Lewis acid present and has proposed a chemical degradation mechanism for PFPEs. He postulated a mechanism in which Lewis acids act as a catalyst that promotes an intramolecular disproportionation reaction, which results in polymer-chain degradation.

Other static degradation studies, conducted to look at the effects of certain metals or metal alloys in the presence of particular PFPEs, have shown that PFPE degradation is highly dependent upon the chemistry of the substrate. For example, an unbranched PFPE lubricant showed more degradation at 288°C in the presence of M-50 steel and Ti-4Al-4Mn than in contact with either pure titanium or pure aluminium [25].

Some studies have applied the concept of modifying one or both of the surface chemistries by coating or ion implantation and observing the associated tribological characteristics. Carré [20] demonstrated that the PFPE, boundary lubricated, wear life was increased by a factor of 5 to 10 by using TiN-coated 440C test specimens. TiC-coated 440C and Si₃N₄ ceramic ball bearings have also been shown to have greater longevity

compared to their 440C counterparts when PFPE lubricated [19-21]. In Carré's studies [20,21] it was concluded that the hard coatings and ceramic material prevented the formation of Lewis acids, thus halting degradation of the PFPE. Shogrin et al. [27] demonstrated that implanting 440C substrates with Ti either with or without a carbon (CH₄) back pressure enhanced the lubricating lifetimes of a PFPE. It was concluded that the resulting microstructures inhibited the formation of reactive sites.

Another way to inhibit tribologically induced degradation may be to passivate the contacting surfaces, which might inhibit the formation of Lewis acids in the presence of fluorinated oils, or decrease the availability of reactive sites on the surface, thus, extending the lubricated lifetime.

The objective of this work was to study the effect of various passivation techniques on the lifetime of PFPE lubricated (Krytox 16256 and Brayco 815Z), 440C stainless steel couples in sliding and rolling contact. Chromic acid passivation (similar to 2,4) and TCP (similar to 1-10), as well as a modified chromic acid passivation technique (which uses a higher temperature and a longer reaction time), and UV/Ozone treatment [28] were studied in sliding contact. TCP and UV/Ozone treatments were also examined in rolling contact. UV/Ozone treatment has been used to remove carbonaceous contamination from surfaces. A demonstration of their effectiveness in prolonging lubricity is sought rather than a detailed description of the associated chemical degradation mechanisms.

EXPERIMENTAL

TRIBOMETERS

Ball-on-disk (BoD)

Tribological testing of each disk/ball couple was performed on the fixed ball-on-disk tribometer shown in Figure 1. All tests were performed using a relative sliding speed of 0.05 m/s and a 3N normal load, which generated an initial Hertzian contact pressure of ~0.69 GPa. Tests were performed in dry N₂ (< 2% RH) at ambient temperature (~25°C). Friction force as a function of disk revolutions (cycles) was recorded for each test.

After a test, the ball was rotated to expose an unworn surface and the fixture was extended so the ball would contact the disk at a different radius.

By doing this, three wear tracks, 1.59 mm (1/16") apart, could be worn on each disk.

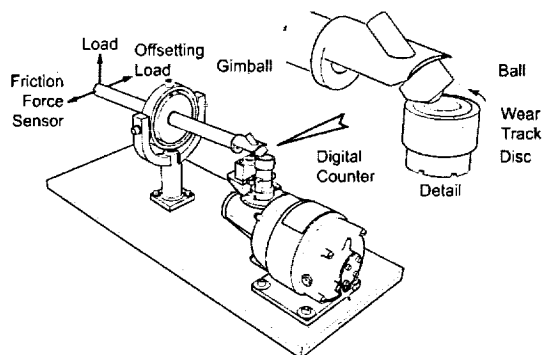


Figure 1 – Ball-on-disk (BoD) tribometer

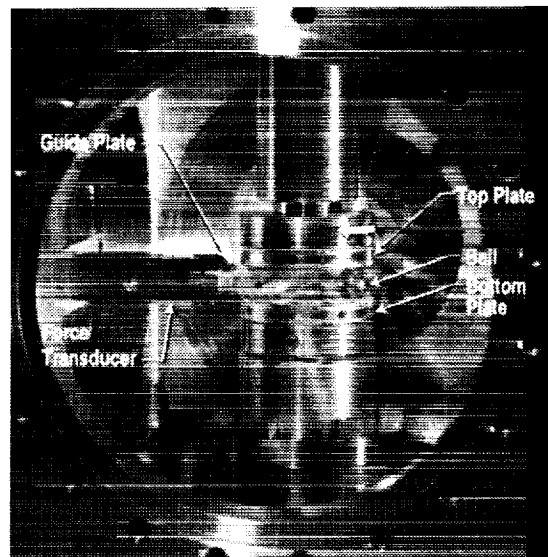


Figure 2 – The spiral orbit tribometer (SOT)

Vacuum Spiral-Orbit-Tribometer (SOT)

Lubricant lifetimes in rolling contact under vacuum were examined using the spiral orbit tribometer (SOT) shown in Figure 2. The SOT is essentially a thrust bearing with a single ball and no retainer. The lower disk is fixed and the top disk rotated. The ball rotates in a spiral orbit and the guide plate is used to return the ball to its original orbit once per revolution. The force the ball exerts on the guide plate is measured and friction force can be calculated. Accelerated testing is achieved by limiting the amount of lubricant available to micrograms, which is completely consumed during the test. Lifetime is defined as the number of orbits before the friction coefficient exceeds a predetermined value. The tribometer is further described in References 29-32 and it previous usages appear in References 33-35.

The effects of TCP passivation and UV/ozone treatment were examined using the SOT. All tests were performed using a mean Hertzian stress of 1.5 GPa, room temperature (~23°C), a vacuum $< 1.3 \times 10^{-6}$ Pa, 200-RPM rotational speed, and 50 µg lubricant.

MATERIALS

Ball on Disk Tribometer

Disks and bearing balls made from 440C stainless steel (fully hardened) were used. The 440C disks were 17.5 mm (11/16") in diameter and 4.76 mm (3/16") thick. Each disk was polished to a mirror finish having an arithmetic roughness average, R_a , of ~ 0.01 µm. The bearing balls were Grade 10 and had a diameter of 9.53 mm (3/8").

Spiral Orbit Tribometer

Disks and bearing balls made from 440C stainless steel (fully hardened) were used. The 440C disks were 50.8 mm (2") in diameter. The disks and guide plate were polished to a mirror finish having an arithmetic roughness average, R_a , of ~ 0.01 µm. The bearing balls were Grade 25 and had a diameter of 12.7 mm (1/2").

Lubricant

The surface preparations tested were: unlubricated and untreated (unpassivated), unlubricated and treated (passivated), and passivated and unpassivated disks that were lubricated. Throughout this report the term "unpassivated" refers to pairs that have not been passivated or

UV/Ozone treated. The lubricant used for the BoD was Krytox 16256. Typical properties of this PFPE are given in Table 1(a). The lubricant used for the SOT tests was Brayco 815Z and its properties are listed in Table 1(b)

Table 1(a) – Selected properties of Krytox 16256

	20°C	50°C	100°C
Vapor Pressure (Torr)	3×10^{-14}	2×10^{-12}	1×10^{-9}
Kinematic Viscosity (cS)	2717	444	63
Density (g/cm ³)	1.92	1.87	1.78
Surface Tension at 25°C	19 dynes/cm		
Average Molecular Weight	11,000 amu		

Table 1(b) – Selected properties of Brayco 815Z

	20°C	100°C
Vapor Pressure (Torr)	4×10^{-13}	2×10^{-9}
Kinematic Viscosity (cS)	249	45
Density (g/cm ³)	1.85	
Average Molecular Weight	9400 amu	

SPECIMEN PREPARATION

Ball on Disk Tribometer

All disk/ball pairs were ultrasonically cleaned in hexane, acetone, and methanol for approximately ten minutes each. The pairs were then blown dry with nitrogen and covered to minimize dust contamination. Disk/ball pairs that were not passivated or lubricated were placed in a N₂ atmosphere (R.H. < 2%) at ambient temperature where they remained until tested. Unpassivated disks that had PFPE applied, were lubricated and then placed in a N₂ atmosphere, with their accompanying unpassivated ball. Disk/ball pairs were treated using one of the four following procedures.

Spiral Orbit Tribometer

The disks and ball were ultrasonically cleaned in hexane, methanol, and distilled water for ten minutes each. The pairs were then rinsed in methanol and blown dry with nitrogen. The disks and ball were treated. The ball was lubricated and then the parts were placed into the vacuum chamber at ambient temperature where they remained until tested. Disks and the ball were treated using one of the four following procedures.

Chromic-Acid Passivation

Clean components were passivated in one of two ways using a solution consisting of 2.0 gm sodium dichromate (Na₂Cr₂O₇·2H₂O), 20 ml concentrated nitric acid (HNO₃), and 80 ml deionized H₂O. Specimens were immersed in the solution either for 30 minutes while heated to 46°C, or for 60 minutes while heated to 56°C. The samples were then removed and thoroughly rinsed using two successive deionized H₂O baths. Samples were then blown dry with nitrogen and covered.

Tricresyl Phosphate (TCP) Passivation

Components were immersed for 48 hours in neat tricresyl phosphate (TCP) heated to 107°C. (The TCP was purchased in accordance with the requirements of TT-T-656b). The samples were then ultrasonically cleaned in hexane, acetone, and methanol for approximately 10 minutes each. Samples were then blown dry with nitrogen and covered.

UV/Ozone Treatment

Disk/ball pairs were UV/ozone treated for 15 minutes to remove carbonaceous contamination [28], which begins to reform immediately after this treatment.

Treated disks that did not have PFPE applied to them, and all treated bearing balls were placed in a dry N₂ atmosphere where they remained until tested. Treated disks that had PFPE applied to them were lubricated (UV/ozone passivated disks were lubricated within 5 minutes of passivation) and then placed in the same dry N₂ environment.

XPS Analysis of Passivated Surfaces

A disk passivated by each of the four techniques and a baseline disk (untreated) were analyzed using X-ray photoelectron spectroscopy (XPS). XPS analyzes the top several atomic layers of the sample providing both elemental and chemical state information. An area of 2 mm x 5 mm was analyzed on each surface. Survey spectra, from 0 to 1200 eV binding energy, were taken to determine which elements were present followed by high-resolution energy windows for each of the major elements detected on the surface to determine their chemical state. There is typically a 5 to 10% error associated with the resulting calculated atomic concentrations.

APPLICATION OF LUBRICANT FILMS

Ball on Disk Tribometer

Thin film deposition was accomplished by using the apparatus shown in Figure 3. This is a derivative of the deposition process known as dipping. In this process, a specimen is lubricated by slowly withdrawing it at a constant speed from a solution of the fluid in a volatile solvent. As the solvent evaporates, a thin film of the non-volatile fluid remains on the surface. In this procedure, both solution concentration and withdrawal speed govern the applied film thickness [36]. For the apparatus used in this study, gravity driven solution flowed past the stationary specimen. The surface speed that the solution attained was approximately 0.8 mm/sec. Each disk was lubricated using a solution with a concentration of 5.0 g of PFPE lubricant in 100 ml of solvent (a perfluorinated cyclobutane).

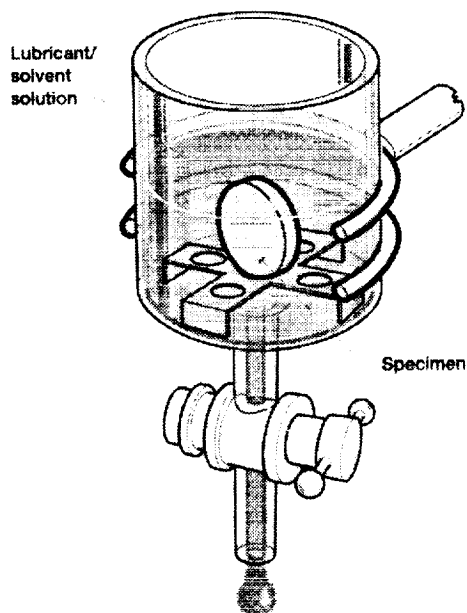


Figure 3 – Film deposition device (FDD)

Spiral Orbit Tribometer

For the SOT tests, only the ball is lubricated with ~50 μg of oil. This uptake is achieved by holding the ball on a fixed point and rotating it while placing

droplets of lubricant dissolved in a solvent on it. As the solvent evaporates, a lubricant film is deposited. The exact lubricant charge is determined by weighing the ball before and after deposition with a sensitive balance. The disks are unlubricated.

LUBRICANT FILM THICKNESS MEASUREMENTS (BALL ON DISK TRIBOMETER)

The PFPE thickness on each disk was measured using an infrared microscope ($\mu\text{-FTIR}$) in the reflectance mode using a Grazing Angle Objective (GAO) with a Mercury Cadmium Telluride (MCT) detector. The instrument's spectral resolution was 4 cm^{-1} . A gold-coated glass slide was used as the background. Absorbance as a function of wave number was determined for each film at three different radii on the disk's surface, approximately 120° apart using an analysis spot diameter of $100\text{ }\mu\text{m}$.

Theoretical thin film optical calculations have been performed to model the PFPE film's behavior in the infrared spectral region [37]. These results are plotted as absorbance of the 1313 cm^{-1} band as a function of film thickness. After experimentally obtaining the absorbance of the 1313 cm^{-1} band, the corresponding film thickness was calculated.

The FDD apparatus produced PFPE film thicknesses of $\sim 400\text{ \AA}$. Lubricant uniformity across any one surface was $\pm 15\%$. The error associated with surface-to-surface film thickness repeatability was $\pm 20\%$.

RESULTS AND DISCUSSION

BALL ON DISK TRIBOMETER

Establishment of the Lubricant-Failure Criterion

Lubricant failure occurred when the friction coefficient increased to a value typical of an unlubricated, unpassivated disk/ball couple. When failure occurred, it was argued that the protective layers (applied lubricant, surface oxide, and/or additional passivation layer) either wore off, ruptured, or broke down. Figure 4 shows the mean friction coefficient as a function of cycle number for three wear tracks on two separate unlubricated, unpassivated couples. Mean friction coefficient was the mean of the friction coefficients of the complete revolution over the indicated cycle. Typically, friction coefficient fluctuations over a

cycle were ± 0.06 (maximum: ± 0.15) about the mean. The mean friction coefficient data all lied between 0.63 and 0.8. Thus, an increase in mean friction coefficient above 0.63 was indicative of failure and was defined as the failure limit. The number of rotational cycles that can be applied to the lubricant film on a wear track before the friction rose above the failure limit was the film's lubricating lifetime.

It was also important to know if the passivation process itself changed the failure limit. Therefore, one disk passivated at each condition was tested unlubricated. Initially, the chromic-acid and TCP passivation samples exhibited lower mean friction coefficients (0.26-0.3), but then raised near linearly above the failure limit at different rates. The value of the TCP passivated surface continued to rise to ~ 0.8 , where it then dropped to a value of ~ 0.53 in the course of one cycle, after which it again rose to failure and stayed. The UV/Ozone treated surfaces showed no improvements and behaved the same as the untreated samples depicted in Figure 5. Table 2 summarizes this data. The UV/Ozone treated results are not shown because no improvements were observed with this technique. In this table, the average values appear outside the parentheses, whereas the ranges are contained within the parentheses. These data suggest that both chromic-acid passivation techniques improved the friction coefficient for a brief time, whereas TCP passivation extended the low friction coefficient for an extended time.

Table 2 – Unlubricated wear test results

Surface Passivation Treatment	Initial Mean Friction Coefficient	No Of Cycles Until Failure	Tracks Tested
Chromic-Acid, Low Temp	0.27 (0.24-0.27)	5 (4-6)	5
Chromic-Acid, High Temp	0.26 (0.24-0.27)	9 (7-10)	4
Tricresyl Phosphate	0.29 (0.27-0.34)	68 (6-85)	5

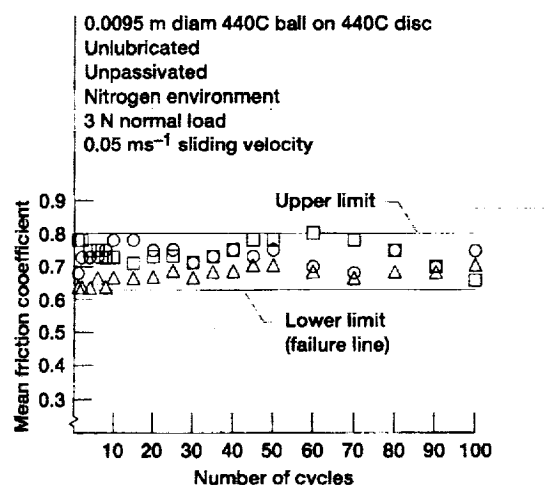


Figure 4 – Typical friction coefficient data for unpassivated, unlubricated disk/ball couples [27]

LUBRICATED RESULTS

Lubricated, unpassivated disks/ball couples were tested. A typical plot of mean friction coefficient vs. cycle number is shown in Figure 5. This data was taken from a disk with a ~ 70 Å PFPE film. The mean friction coefficient begins to rise from ≤ 0.3 near 200 cycles and crosses the failure line of 0.63 at ~ 370 cycles (lubricant lifetime = 370 cycles).

This general trend was typical for the samples used in this study. In these tests the maximum variation of the friction coefficient before it began to rise (here at ~ 200 cycles) was ± 0.02 . The relatively small variation indicated that the entire wear track was uniformly experiencing the benefits of full boundary lubrication from the PFPE. After the initial rise, the variation of friction coefficient grew as the number of cycles increased until, at the failure limit, it typically had a variation of ± 0.1 (maximum: ± 0.20 , minimum: ± 0.03).

As a test progressed, different locations on the wear track lost their lubricity at varying rates, which accounted for the spread in friction coefficient values seen over one cycle (indicated by the variation noted above). Although the rate of lubricity loss over the entire wear track varied, and the variation increased as the number of cycles increased, the mean friction coefficient continued to rise, signifying an overall loss of lubricity.

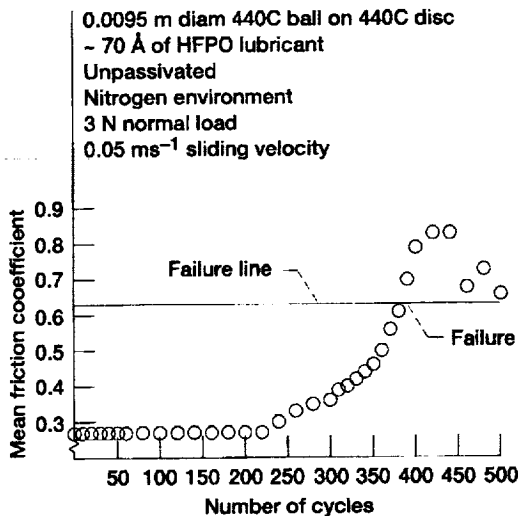


Figure 5 – Typical friction coefficient data for unpassivated, lubricated disk/ball couples [26]

Beyond failure, variations of the friction coefficient over a rotational cycle, as well as the mean friction coefficient were sporadic. On some wear tracks, the mean friction coefficient dipped below the failure line after it had reached failure (rarely dipping below ~0.4). This decrease was caused by the rapid growth of the wear scar's width coming into contact with fresh, unused PFPE lubricant. This fresh lubricant decreased the friction coefficient before it too degraded, causing the mean friction coefficient to again rise above the failure limit. These sporadic variations were also considered an indicator of failure.

After performing a number of the tests, it was apparent that the lifetimes had a significant spread in their values for each of the unpassivated and passivated conditions. These spreads in lifetime appeared random, as they were not dependent upon either a particular disk or radius of wear track. Weibull statistics [38] were used to characterize this data.

The Weibull plot for the unpassivated disk/ball couples lubricated with Krytox 16256 is shown in Figure 7. Each data point represents the lubricated lifetime of one wear track. The Median Rank Line represents the most probable failure history for the samples, that is, the fraction of a group of samples

that can be expected to fail (i.e. exceed 0.63 friction coefficient) as a function of the number of sliding cycles. This line suggests 60% of a given number of tests can be expected to undergo failure at or before ~3700 cycles. Given an infinite number of tests, the 90% confidence bands were in the region in which the lifetimes of 90% of those tests would reside.

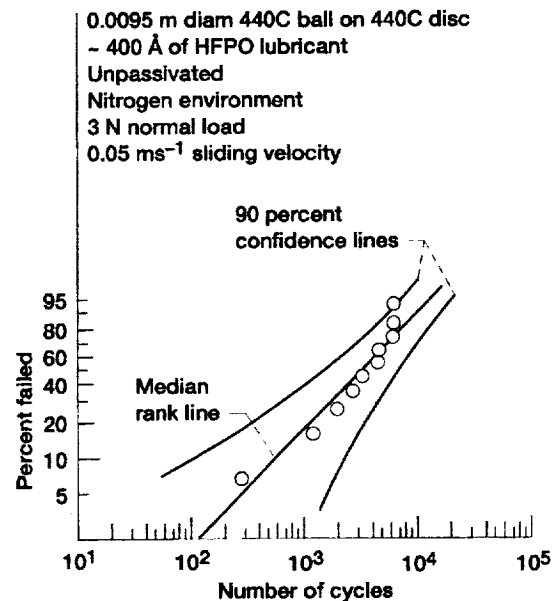


Figure 6 – Weibull distribution lifetimes for unpassivated, lubricated disk/ball couples

The usefulness of a Weibull plot can be demonstrated by relating it to the reliability of a component. For a typical space bearing, which cannot generally be retrieved for maintenance, reliability is very important. If greater than 99% reliability is desired in a lubricated couple, then the number of cycles that it is allowed to experience should be less than the value that will generally produce failure 1% of the time. For the unpassivated samples in Figure 6, 1% of them are predicted to fail by ~120 cycles. By comparing each passivation technique's Weibull plot to the plot of the unpassivated specimens (Figure 6), and to each other, produces their relative performance. Their relative performance is summarized after the next section.

PASSIVATED - LUBRICATED RESULTS

The Weibull lifetime distributions of the four passivation techniques and the unpassivated technique (from Figure 6) are shown in Figure 7. This figure indicates that the predicted lifetimes are all very similar. The 90% confidence bands of the five plots (not shown) all overlap over most of the range of each Median Rank Line. Therefore, within 90% assurance, it is predicted that no one passivation technique out performs another. These plots indicate that none of the passivation techniques exhibited superior or grossly sub-standard performances relative to the unpassivated surfaces.

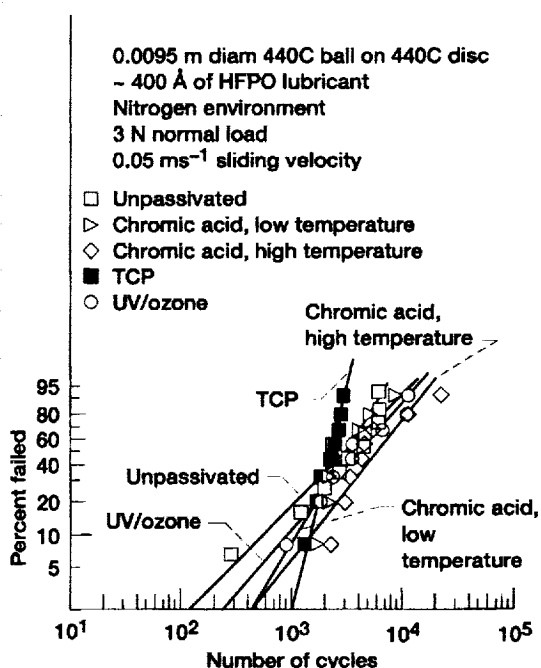


Figure 7 – Effect of passivation on Weibull distribution lifetimes for lubricated disk/ball couples

The 1% and 60% predicted lifetimes are tabulated in Table 3. Again, statistically one cannot say that any one technique out performed another. The possible exception to that may be the 1% failure lifetimes. TCP passivated samples have a 1% failure of ~1000 cycles, which is nearly an order of magnitude higher than that of the unpassivated result of ~120 cycles. This difference is caused by the greater slope (more reproducible data) of the TCP passivated samples. More tests would have to be run to verify this possible distinction.

Given the sliding nature of these tests and the thinness of both the lubricant and the passivation layers, one might have predicted this result. However, the unlubricated tests did show measurable differences between the various techniques. In addition, this same procedure was used to evaluate differences in various ion-implanted surfaces [27]. The thicknesses of the implanted layers were of the same order as the thicknesses of the passivated layers. Finally, it has been known for decades that the TCP presoak and the low temperature chromic acid passivation techniques provide additional protection in boundary lubricated contact while lubricated with either mineral oils or esters [1-10]. Thus, the authors conclude that none of the passivation techniques tested increased the longevity of the perfluoropolyether (16256) lubricated wear couples.

Table 3 – Summary of data from Weibull plots

Surface Passivation/Treatment	1% Failure	60% Failure
Unpassivated	120	3700
Chromic-Acid, Low Temp	440	3600
Chromic-Acid, High Temp	440	7000
Tricresyl Phosphate	1000	2300
UV/Ozone Treatment	240	5000

XPS ANALYSIS OF THE PASSIVATED SURFACES

By using XPS oxide-to-metal peak area ratios, it was estimated that the oxide film thickness for all the surfaces (Cr_xO_y , Fe_xO_y or FePO_4) was less than ~50 Å. A summary of the atomic percent of selective elements obtained from the XPS analysis of a surface passivated using each of the four techniques and the unpassivated surface is shown in Table 4. The unpassivated surface had Cr to Fe ratio of 0.34, and a distinct carbonaceous contaminating layer as indicated by the C atomic percent.

The low temperature chromic-acid passivated sample had a high Cr/Fe ratio (2.3). This indicates that the passivation solution selectively attacked and dissolved the near-surface iron oxide, while leaving the more inert chromium oxide intact. This would account for the change in Cr to Fe ratio in the first few atomic layers of the surface. The higher nitrogen atomic percent on this surface was caused by the nitric acid.

The surface of the sample passivated with the high temperature chromic-acid solution has a lower Cr to Fe ratio than the low temperature chromic-acid passivated surface, but a higher ratio than the unpassivated surface. The difference in the Cr to Fe ratios for the two passivation techniques is considered to be within the random error associated with the passivation procedure. It is noted that the two passivation techniques resulted in very similar surface chemistries, which indicates that increasing the passivation time and temperature was relatively ineffective. The fact that the Cr to Fe ratio is higher than the unpassivated surface indicates that the Fe atoms are being selectively removed at a higher rate than the Cr atoms.

Table 4 – Elemental surface concentration for each passivating treatment obtained by XPS

Atomic % of	C	O	Fe	Cr	Cr/Fe Ratio	Misc.
Unpassivated	28	54	13	4.4	0.34	0.5N
Chromic-Acid, High Temp	23	61	4.3	10	2.30	0.9N
Chromic-Acid, Low Temp	19	61	10.1	9.3	0.93	0.9N
Tricresyl Phosphate	24	58	4.6	1.1	0.24	0.8Na 3.5Ca 12P
UV/Ozone Treatment	18	58	18	6	0.33	<0.1N

Evidence for iron phosphate formation from TCP passivation is shown in Figure 9. The figure compares the XPS spectra of the Cr region of the high-temperature chromic-acid passivated surface to that of the TCP passivated surface. The chromic-acid passivated surface has a large $\text{Cr}^{3+}:\text{Cr}^0$ metal peak, whereas, the TCP passivated spectra contains a much smaller $\text{Cr}^{3+}:\text{Cr}^0$ metal peak. This, along with the presence of the 12 atomic percent P, and the decreased Cr to Fe ratio are consistent with the formation of an iron phosphate surface layer.

As evidenced by a decrease in carbon on the UV/ozone treated surfaces, UV/ozone treatment preferentially removes the carbonaceous contamination layer. UV/ozone treatment was not found to increase the oxide film thickness of these samples. This fact has been previously documented [28].

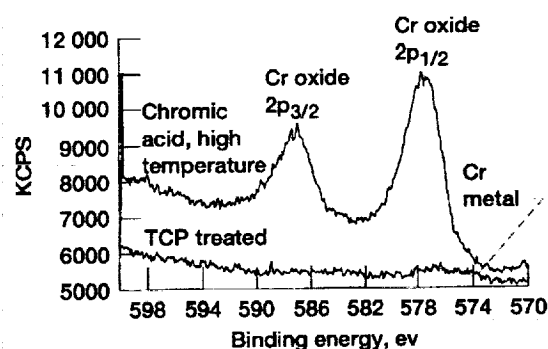


Figure 9 – XPS spectra showing the chromium oxide region of both the high temperature chromic-acid and TCP passivated surfaces

SPIRAL ORBIT TRIBOMETER

The SOT results also showed no difference in lubricated lifetime of Brayco 815Z when comparing the TCP passivated surface to the UV/Ozone treated surface. Lifetime for the UV/Ozone test was 57 ± 28 orbits per microgram vs. 64 ± 42 orbits per microgram for the TCP passivated surfaces. The SOT mimics the operating parameters of a real bearing operating in the boundary lubrication regime. These results support the conclusion that none of the passivation techniques tested increased the lubricated lifetimes using perfluoropolyethers.

SUMMARY OF RESULTS

1. None of the passivation techniques significantly increased the oxide film thickness.
2. Using X-ray photoelectron spectroscopy, it was found that chromic acid passivation increased the Cr to Fe ratio of the surface. Couples passivated with chromic acid, tested unlubricated, experienced an improvement in friction coefficient for a short time. However, chromic acid passivation did not affect the PFPE lubricating lifetime.
3. TCP passivation resulted in a few-monolayer-thick FePO_4 layer on the surface. TCP passivated couples tested unlubricated, experienced improved, low friction for a short duration. However, an improvement in PFPE-lubricating lifetime was not observed after TCP passivation.
4. UV/Ozone treatment removed the carbonaceous contamination layer on the surface but did not alter either the unlubricated or the PFPE-lubricated lifetimes.

CONCLUSIONS

1. The PFPE lubricated lifetime (Krytox 16256) of sliding 440C couples did not statistically change as a result of the various passivation techniques.
2. The PFPE lubricated lifetime (Brayco 815Z) of 440C couples in boundary lubricated rolling contact did not statistically change as a result of the TCP passivation technique.

REFERENCES

1. Singer, H.B., "The Effect of TCP Treatment on the Low-Speed Performance of Ball Bearings," MIT/IL E-2317, Sept 1968; presented at the Dartmouth Bearings Conference, Dartmouth College, Hanover, N.H., 3-6 Sept 1968.
2. Allen, S., "Effect of Surface Condition of Instrument Ball Bearings," *Proc. Int'l. Conf. Surf. Techn.*, pp 566-583, 1973.
3. Singer, H.B., "A Potpourri of Ball Bearing Surface Chemistry Problems," Charles Stark Draper Laboratory, Cambridge, MA, Rept. P-1474, 1982. Presented at the Seventh Contamination Symposium, Sunnyvale, CA, 1982.
4. Murday, J.S., Shafrin, E.G., Kingsbury, E.P., and Allen, S., "Surface Chemistry of Ball Bearing Steels I," NRL Memorandum Report 3047, April, 1975.
5. Shafrin, E.G., and Murday, J.S., "Auger Compositional Analysis of Ball Bearing Steels Reacted with Tricresyl Phosphate," *ASLE Trans.*, **21**, 4, pp 329-336, 1978.
6. Shafrin, E.G., and Murday, J.S., "Analytical Approach to Ball-Bearing Surface Chemistry," *J. Vac. Sci. Technol.*, **14**, 1, Jan/Feb 1977.
7. Allen, S., "Final Report, Gyro Bearing Program, Tasks 1 to 6, NAS 9-3079," MIT/DL R-586, June 1970; "Tasks 8 to 10, NAS 9-3079," MIT/DL R-674, Oct 1970.
8. Woodwell, R.G., Miller, L., and Anderson, C., "Alkaline Cleaning: Its Effects on Tricresyl Phosphate Coated Bearing Steels," presented at the Non-Ozone Depleting Chemical Cleaning and Lubrication of Space System Mechanical Components for Multi-Year Operations, Pub. No. S69-5762-1.0-1, Sept 26-27, 1994.
9. Edwards, A.C., "Final Report on the Gyro Spin-Axis Bearing Program," MIT/IL R-418, Sept 1963.
10. Hannan, C.H., "The Effect of Tri-Cresyl-Phosphate Coating on Reducing Torques in Low-Speed Bearings," presented at the Dartmouth Bearings Conference, Dartmouth College, Hanover, N.H., 3-6 Sept 1968.
11. Wedeven, L.D. and Goodell, A.J., "Evaluation of Passivated and TCP Treated 440C Surfaces with WA Machine," Wedeven and Assoc., Subcontract No. SS-274275-J, Sept. 1991.
12. Jones, W.R., Jr., "Properties of Perfluoropolyethers for Space Applications," *Trib. Trans.*, **38**, 3, 557, 1995.
13. Fleischauer, P.D., and Hilton, M.R., "Assessment of the Tribological Requirements of Advanced Spacecraft Mechanisms," TOR-0090 (5064)-1, 1991.
14. Rowntree, R.A., and Todd, M.J., "A Review of European Trends in Space Tribology and Its Application to Spacecraft Mechanism Design," *Mat. Res. Soc. Symp. Proc.*, **140**, 21-34, 1989.
15. Watson, N.D., Miller, J.B., Taylor, L.V., Lovell, J.B., Cox, L.W., Fedors, J.C., Kopia, L.P., Holloway, R.M., and Bradley, O.H., "Earth Radiation Budget Experiment (ERBE) Scanner Instrument Anomaly Investigation," NASA TM-87636, 1985.
16. Conley, P.L. and Bohner, J.J., "Experience with Synthetic Fluorinated Fluid Lubricants," 24th Aerospace Mech. Symp., NASA CP-3062, pp 213, 1990.
17. Herrera-Fierro, P., Jones, W.R., Jr., and Pepper, S.V., "Interfacial Chemistry of a Perfluoropolyether Lubricant Studied by X-ray Photoelectron Spectroscopy and Temperature Desorption Spectroscopy," *J. Vac. Sci. Technol. A*, **2**, 11, Mar/Apr 1993.
18. Carré, D.J., "Perfluoropolyalkylether Oil Degradation: Inference of FeF₃ Formation on Steel Surfaces Under Boundary Conditions," *ASLE Trans.*, **29**, 2, 121-125, 1986.
19. Hayashida, K., Yamamoto, K., and Nishimura, M., "Wear and Degradation Characteristics of Perfluoroalkylpolyethers (PFPEs) in High Vacuum," *Trib. Trans.*, **37**, 1, 196-200, 1994.
20. Carré, D.J., "The Use of Solid Ceramic and Ceramic Hard-Coated Components to Prolong the Performance of Perfluoropolyalkylether Lubricants," *Surf. and Coat. Tech.*, **43/44**, pp 606-617, 1990.
21. Carré, D.J., "The Performance of Perfluoropolyalkylethers Under Boundary Conditions," *Trib. Trans.*, **31**, 4, 437-441, 1988.
22. Mori, S., and Morales, W., "Tribological Reactions of Perfluoroalkylpolyether Oils with Stainless Steel Under Ultrahigh Vacuum Conditions at Room Temperature," *Wear*, **132**, 111-121, 1989.
23. Kasai, P.H., "Perfluoropolyethers: Intramolecular Disproportionation," *Macromolecules*, **25**, pp 6791-6799, 1992.
24. Carré, D.J., and Markowitz, J.A., "The Reaction of Perfluoropolyalkylether Oil with FeF₃, AlF₃, and AlCl₃ at Elevated Temperatures," *ASLE Trans.*, **28**, 1, pp 40-46, 1985.
25. Jones, W.R., Jr., Paciorek, K.J.L., Harris, D.H., Smythe, M.E., Nakahara, J.H., and Kratzer, R.H., "The Effects of Metals and Inhibitors on Thermal Oxidative Degradation Reactions of Unbranched Perfluoroalkylethers," *R. H. Ind. Eng. Chem. Prod. Res. Dev.*, **24**, pp 417-420, Sept. 1985.
26. Morales, W., "Perfluoropolyalkylether Decomposition on Catalytic Aluminas," NASA TM-106547, Apr 1994.
27. Shogrin, B., Wilbur, P.J., Jones, W.R., Jr., Herrera-Fierro, P., and Williamson, D.L., "The Effects of Ion Implantation on the Tribology of Perfluoropolyether-Lubricated 440C Stainless Steel Couples," *Tribology Transactions*, **39**, 3, pp 507-516, 1996.

28. Vig, J.R., "UV/Ozone Cleaning of Surfaces," SLCET-TR-86-6, May 1986.
29. Pepper, S.V., Kingsbury, E., Ebihara, B.T., "A Rolling Element Tribometer for the Study of Liquid Lubricants in Vacuum," NASA TP-3629, October 1996.
30. Brown, P.L., Miller, J.B., Jones, W.R., Jr., Rasmussen, K., Wheeler, D.R., Rana, M., Peri, F., "The Clouds and the Earth's Radiant Energy System Elevation Bearing Assembly Life Test," 33rd Aero. Mech. Symp., Pasadena, California, NASA CP 1999-209259, pp 197-212, 1999.
31. Loewenthal, S.H., Jones, W.R., Jr., Predmore, R.E., "Life of Pennzane and 815-Z Lubricated Instrument Bearings Cleaned with Non-CFC Solvents," NASA TM 1999-209392, September 1999.
32. Jones, W.R., Jr., Pepper, S.V., Jansen, M.J., Nguyen, Q.N., Kingsbury, E.P., Loewenthal, S.H., Predmore, R.E., "A New Apparatus To Evaluate Lubricants for Space Applications – The Spiral Orbit Tribometer (SOT)," NASA TM 2000-209935, March 2000.
33. Kingsbury, E., "Evaluation of the NASA Ball on Plate Tribometer as an Angular Contact Ball Bearing", *Proc. Inter. Roll. Elem. Bear. Symp.*, REBG, Orlando, FL, April 28-30, 1997.
34. Pepper, S.V., Kingsbury, E., "Destruction of Fomblin Z-25 by Different Bearing Metals," *Proc. Inter. Roll. Elem. Bear. Symp.* REBG, Orlando, FL, April 28-30, 1997.
35. Jansen, M.J., Jones, W.R., Jr., Wheeler, D.R., Keller, D.J., "Evaluation of Non-Ozone-Depleting-Chemical Cleaning Method for Space Mechanisms Using a Vacuum Spiral Orbit Rolling Contact Tribometer," NASA TM 2000-210050, May 2000.
36. Scarati, A.M., and Caporiccio, G., "Frictional Behaviour and Wear Resistance of Rigid Disks Lubricated with Neutral and Functional Perfluoropolyethers," *IEEE Trans. on Magnetics*, Mag., **23**, 1, pp 106-108, Jan. 1987.
37. Pepper, S.V., "Characterization and Application of a Grazing Angle Objective for Quantitative Infrared Reflection Spectroscopy," *Appl. Spect.*, **49**, 3, pp 354-360, March 1995.
38. Johnson, L.G., The Statistical Treatment of Fatigue Exper., Elsevier Publishing Company, Inc., 1964.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 2001		3. REPORT TYPE AND DATES COVERED Technical Memorandum
4. TITLE AND SUBTITLE The Effects of Acid Passivation, Tricresyl Phosphate Presoak, and UV/Ozone Treatment on the Tribology of Perfluoropolyether-Lubricated 440C Stainless Steel Couples			5. FUNDING NUMBERS WU-274-00-00-00	
6. AUTHOR(S) Bradley A. Shogrin, William R. Jones, Jr., Pilar Herrera-Fierro, and Mark J. Jansen				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration John H. Glenn Research Center at Lewis Field Cleveland, Ohio 44135-3191			8. PERFORMING ORGANIZATION REPORT NUMBER E-12801	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA TM-2001-210947	
11. SUPPLEMENTARY NOTES Prepared for the Second World Tribology Congress sponsored by The Society of Tribologists and Lubrication Engineers, Vienna, Austria, September 3-7, 2001. Bradley A. Shogrin, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109; William R. Jones, Jr., NASA Glenn Research Center; Pilar Herrera-Fierro, Energy Conversion Devices, 1621 Northwood Drive, Troy, Michigan 48084; and Mark J. Jansen, AYT Corporation, 2001 Aerospace Parkway, Brook Park, Ohio 44142. Responsible person, William R. Jones, Jr., organization code 5960, 216-433-6051.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified - Unlimited Subject Category: 27 Available electronically at http://gltrs.grc.nasa.gov/GLTRS This publication is available from the NASA Center for AeroSpace Information, 301-621-0390.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The boundary-lubrication performance of two perfluoropolyether (PFPE) thin films in the presence of passivated 440C stainless steel is presented. The study used a standard ball on disk (BoD) tribometer in dry nitrogen and a vacuum spiral orbit tribometer (SOT). Stainless steel surfaces were passivated with one of four techniques: high and low temperature chromic acid bath, a tricresyl phosphate (TCP) soak, or UV/Ozone treated for 15 min. After passivation, each BoD disk had a 400Å film of Krytox 16256 (PFPE) applied to it. The lifetimes of these films were quantified by measuring the number of sliding cycles before an increase in friction occurred. The lubricated lifetime of the 440C couple was not altered as a result of the various passivation techniques. The resulting surface chemistry of each passivation technique was examined using X-ray photoelectron spectroscopy (XPS). The SOT was used to examine the effects of the TCP treatment on the lubricated lifetime of another PFPE, Brayco 815Z, under rolling conditions. None of the passivation techniques were found to dramatically increase the oxide film thickness or lubricated lifetimes.				
14. SUBJECT TERMS TCP; Perfluoropolyether; Passivation			15. NUMBER OF PAGES 17	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	